

Role of Water Activity in Food Stability

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Water activity, a thermodynamic parameter, is the ratio of vapor pressure of water in a system to that of pure water at the same temperature or equilibrium relative humidity of surrounding air. It plays a pivotal role in microbial growth inhibition and material stability. The influence of water activity (a_w) on molecular mobility within the matrix affects physical stability, primarily governed by diffusion, a kinetic process influenced by factors like matrix porosity and molecular sizes. Water activity is a vital factor in microbial growth and food shelf life. It significantly impacts food quality, stability, and safety, influencing deteriorative reactions, physical attributes, and microbial growth rates. Methods like concentration, dehydration, and freezing decrease water availability for microbial activity. Additionally, preservation techniques involving solutes restrict microbial water access, further enhancing food stability and safety.

Importance of water activity (a_w) and Growth of Microbes in Foods

The majority of food contains more water than 0.95, which promotes the growth of bacteria, yeast, and mold. It is important to understand a food's water activity when establishing a Hazard Analysis Critical Control (HACCP) plan. When performing a hazard analysis for many items, evaluating the water

activity of a product or substance is required. At water activities below 0.8, the majority of enzyme processes are slowed down. During storage, a_w also has an impact on the uniformity, flow and caking of milk powder and other powdery food ingredients. The texture characteristics of food are also affected by a_w .

Hysteresis

Hysteresis, or the difference in equilibrium moisture content between the adsorption and desorption curves, is illustrated in Figure 1. Because a substance could exhibit two different a_w values at a given water content, two different paths between the adsorption and desorption isotherms are observed. The reason for this is due to a given meal, different amounts of adsorption and desorption may occur at the same vapor pressure. Situated above the adsorption isotherm is the desorption isotherm. Different hysteresis loop shapes appear depending on the food type and isotherm temperature. Further factors influencing hysteresis include product composition, period of storing before isotherm testing, drying time, etc. Although the water usually exists in small capillaries in region II of this figure, it is held less tightly in region III and is either free or held loosely in large capillaries by Fortes *et al.*, (1980). Foods are affected both theoretically and practically by sorption hysteresis. The theoretical

implications show that the sorption process is irreversible and that the equilibrium thermodynamic process is correct. Hysteresis' importance for low- and intermediate-moisture foods, as well as its impacts on chemical and microbiological deterioration, are covered in the practical implications by Kapsalis *et al.*, (1987). Since food hysteresis loops alter with storage time, Strasser *et a.*, (1969) and Wolf *et al.*, 1972 suggested that changes in hysteresis may be utilized as an indication of quality deterioration.

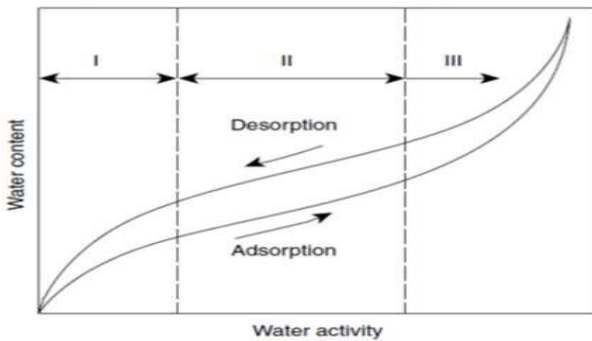


Fig. 1 Water Sorption Isotherm Showing a Hysteresis Loop

Water Activity in Food Preservation

Brunauer-Emmet-Teller (BET) Equation

Water activity in food preservation relies on the monolayer concept. The Brunauer-Emmett-Teller (BET) isotherm, developed by Brunauer, Emmet, and Teller in 1938, is used to determine the monolayer value, crucial for assessing food stability. The BET equation can be derived using kinetic, statistical mechanics, or thermodynamic principles. Formula for the equation:

$$\frac{a_w}{(1 - a_w)m} = \frac{1}{M_o C} + \frac{(C - 1)a_w}{U_o C}$$

where M_o is the monolayer moisture content, C is the constant related to the net heat of sorption. The above equation can be rewritten in linearized form as

where $\alpha = [(C-1)/(M_o C)]$ and $\beta = 1/(M_o C)$.

α is determined from the slope and β is determined from the intercept of the straight line when $[a_w/(1 - a_w)M]$ is plotted as a function of a_w .

The monolayer moisture content (M_o) and the net heat of sorption (C) parameters are then determined.

Above the upper limit of 0.5 a_w , the results deviate from the straight-line portion when plotted as a linear equation. For type II isotherms, the value of 'C' varies from 2 to 50. When Q_s is very large, as in the case of chemisorption (type I isotherm), the value varies from 50 to 200, whereas for type III isotherms representing crystals, Q_s approaches 0 and the constant 'C' is less than 2. Note that the model does not predict adsorption in the capillary region (Region 3 of the isotherm). The BET equation provides the value of monolayer moisture content. Evaluating water uptake at the monolayer value is important because it determines the level of moisture content at which dehydrated foods can be preserved with the least amount of deterioration due to adsorption and interaction of adjacent polar groups.

The monolayer value usually ranges from 0.2 to 0.4 in terms of water activity by Labuza (1984). Additionally, the BET monolayer computation is a useful technique for determining the amount of bound water at particular polar places in dehydrated food systems McLaren *et al.*, (1952) For foods and food components, the BET monolayer values typically range from 0.01 to 0.14 (dry basis). High fat food

including avocado, peanuts, and whole milk showed lower BET monolayers than macromolecules like starch, protein, and agar, which typically have greater monolayers. After evaluating 100 foods and dietary components, Iglesias and Chirife (1976) showed that monolayer values became significant with rising temperatures. This could be because higher temperatures enhance gas molecules' propensity to escape, based on thermodynamics.

Guggenheim-Anderson-de Boer (GAB) model

Rahman (1995) has obtained the monolayer values and GAB model parameters for a variety of food items. While GAB offers greater mathematical isotherm prediction across a wide variety of water activities, it is important to acknowledge that the BET monolayer is used for food stability. The equation was independently developed by Guggenheim (1966), Anderson (1946) and de Boer (1968) and is shown below

$$\frac{m}{M_o} = \frac{CKa_w}{(1 - Ka_w)[1 - Ka_w + CKa_w]}$$

C' and 'k' are constants associated with the energies of interaction between the first and the distant sorbed molecules at the individual sorption sites. Mo is the GAB monolayer value. The GAB equation reduces to the BET equation when K = 1. This constant 'K' permits the model to be applicable to higher water activity (at multilayer moisture region). All of the parameters used in GAB equation have physical meaning associated with them.

Methods for Control of Aw and Moisture

Dehydration: is the process in which water is transferred from a food to a gas or air. The gas is then recirculated or allowed to escape.

Spray-Drying: The liquid or slurry is finely atomized and introduced into the drying chamber, where it is brought into contact with a gaseous heating medium such as air. Air transfers the heat to the individual spray particles, evaporating the moisture and leaving the solids as a powder floating in the air stream. The fine droplets of 10-200 microns present a very large surface area per unit volume. Very rapid drying (1-30 s) occurs because of the vast surface area. The product particles may never reach a temperature higher than the wet-bulb temperature of the air. Hence, minimum damage occurs to the product even though higher air temperatures are used for drying. Most of the drying occurs under constant rate drying conditions. The air stream in spray dryers may be co- or counter-current, with a variety of air-flow patterns.

Drum Drying: Ideal for slurries, pastes and solutions. The material to be dried is spread onto the surface of the drum and heated by condensing steam inside the drum. The heat is transferred to the product through the metal thickness of the drum. Drums varying from 0.3 to 3 m in diameter are used. The surface temperature of the drums may be much higher than that of the product film due to evaporative cooling. The speed of revolution of the drum is 1-5 rpm, while the dried product is in contact with the drum for less than one complete revolution. Properties that affect drum adherence are viscosity, surface tension, and wetting power. The product is distributed over the drum surface by splash or dip feeders. The time of drying is in seconds. The dried product is removed using a doctor's blade as a continuous sheet. The capacity of a drum dryer is a function of the drying rate of the thin layer of material and the amount of product that adheres to the drum surface. The drying

rate depends on the type of feed device, steam pressure within the drum, and the drum speed. Drum drying is relatively inexpensive and efficient, but may yield products with burnt flavor.

Belt and Tunnel Dryer: Both types of dryers are very similar in design except that in belt dryers, the product is distributed uniformly to a thickness of 30-150 mm on a porous belt through which air circulates in an upward or downward pattern. In the tunnel dryer, layers of food are dried on trays, which are stacked on carts or trucks programmed to move at a specified rate in a tunnel. The airflow in the tunnel is horizontal and may be co- or counter current. The final finishing of the product is done in bin dryers. Both dryers have the ability to dry large quantities of material within relatively short times.

Fluidized Bed Drying: Commonly used for drying potatoes, peas, carrots and selected vegetables. The moist product is introduced continuously at one end onto a grate or porous plate. Beneath the grate lies the air distributor and heater, from which hot air is blown up. As the product moves slowly over this plate in a continuous bed, it becomes gently suspended by the hot air, which facilitates mixing and faster drying. The rapid mixing of the product provides nearly isothermal drying conditions. The air exhaust system is connected to a dust recovery system and an exhaust fan. The bed depth is not greater than the bed diameter.

Freeze Drying: In freeze-drying, water is sublimed directly from ice crystals in the frozen product and the ice is not allowed to melt. The frozen food is placed on heated shelves within a vacuum chamber, and heat is applied to the shelf to provide the latent

heat of sublimation by conduction or radiation. The sublimed ice, now as a vapor, is pulled from the vacuum chamber by vacuum pumps or steam jet ejectors. As sublimation proceeds, the ice front within the food recedes at a progressively slower rate. The final moisture content may be approximately 2-8%. Principal advantages are the elimination of product shrinkage, improved flavour and colour retention, and superior rehydration characteristics.

Conclusion

To prevent the growth of microorganisms and enhance the shelf life of dairy products, it is essential to determine the water activity of food and dairy products. Most foods are spoiled due to higher water activity causing oxidation, non-enzymatic browning, and hydrolytic rancidity and bacteria, yeast and mold growth. The preservation of foods based on water activity to retard the growth of microorganisms and also extend the shelf life of foods. The water activity in food preservation is using the two equations as Brunauer-Emmet-Teller (BET) Equation concept and Guggenheim-Anderson-de Boer (GAB) model that is based on the monolayer and food stability diagram. The methods used to control the water activity and to prevent the growth of microorganisms such as freeze drying, dryers, concentrations and dehydration process.

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Table 1. Limiting Water-activity for Microorganisms in Different Food Products

Food Products	Water activity (a _w)	Inhibited microorganisms
Highly perishable (fresh) foods as well as canned fruits, vegetables, meat, fish, and milk; foods containing with up to 40% (w/w) sucrose or 7% sodium chloride	1.00–0.95	Pseudomonas, Escherichia, Proteus, Shigella, Klebsiella, Bacillus, Clostridium perfringens, some yeasts
Certain foods containing 65% (w/w) sucrose (saturated) or 15% sodium chloride; sponge cakes; dry cheeses; margarine; and fermented sausages	0.91–0.87	Micrococcus and many yeasts
Most fruit juice concentrates; sweetened condensed milk; flour; rice; pulses containing 15–17% moisture	0.87–0.80	Most molds, Staphylococcus aureus, most Saccharomyces (bailii) spp., Debaryomyces
Jam, marmalade	0.80–0.75	Most halophilic bacteria, mycotoxigenic aspergilli
Rolled, oats, fudges marshmallows, jelly, some dried fruits, and nuts containing 10% moisture	0.75–0.65	Xerophilic molds, Saccharomyces bisporus
Dried fruits containing 15–20% moisture; honey	0.65–0.60	Osmophilic yeasts, few molds
Pasta and spices containing 12% and 10% moisture	0.50	No microbial proliferation
